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Inventor: Suminov, Igor Vjatsjeslavovits  
ul. Sjtsjerbakovskaja, d.8-12, kv.55  
Moscow (RU)

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Inventor: Epelfeld, Andre Valerjevitsj  
Leningradskoje sjoss d.9 k.2, kv.326  
Moscow(RU)

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Inventor: Fjodorov, Jevgenij Aleksandrovitsj  
Ul. Verchojanskaja, d.6, k.1, kv.63  
Moscow(RU)

71 Applicant: Hauser, Franciscus Johannes  
Matheus  
Koelderstraat 21  
NL-5916 NH Venlo(NL)

74 Representative: Morgan, James Garnet  
et al

72 Inventor: Mittin, Boris Sergejevitsj  
ul. Mikloecho-Kaklaja, d.41, kv.113  
Moscow (RU)

Manitz, Finsterwals & Rotermund  
Patent attorneys  
P.O. Box 22 16 11  
D-80506 Munich (DE)

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54 Method for electrolytic coating of substrates and the like.

57 A method for electrolytic coating of substrates or the like is described, in which the substrate is dipped into an electrolytic bath and a current is generated between the substrate forming a first electrode and a second electrode. The electrode voltage is first boosted to a value in which an electric spark and microarc discharge ensues on the substrate surface. The electrode voltage is continuously increased during the coating buildup supported by the electrical discharge, until the desired coating thickness has been achieved.

The invention relates to a method for electrolytic coating of substrates or the like, in which the substrate is dipped into an electrolytic bath and a current is generated between the substrate forming a first electrode and a second electrode, whereby the pulsed electrode voltage is boosted to a value in which an electric spark discharge and microarc discharge ensue on the substrate surface.

In a method of this kind known from US 4 082 626 silicate coatings are applied to semiconductor metals or their alloys using a corresponding electrolytic bath. In this method the metal to be coated is used as an anode. A further electrode also subjected to the electrolytic bath serves as a cathode. The electrode voltage is first increased until a visible spark discharge ensues. The electrode voltage is boosted to about 300 V and during the coating buildup kept at this voltage value until achievement of the desired coating thickness.

With this known method it is possible to manufacture well-holding, relatively hard, glass-like and corrosion-proof coatings. However, under the given conditions it is not possible for example to get relatively thick, dielectric coatings that are also resistant to wear.

A method for manufacturing decorative coatings on the barrier layer forming metals of aluminum, titanium, zirconium, niobium, tantalum or their alloys is known from EP 0 280 886 B1, whereby a pulse voltage-determined electrochemical and plasma chemical anodic reaction is performed in an aqueous electrolyte by means of special parameter selection in such a way that decorative layers can result with a homogenous thickness of 3  $\mu\text{m}$  to 30  $\mu\text{m}$ .

For pulse operation in particular pulses with needle-pulse character are recommended, in order to achieve a uniform layer thickness with only slight roughness, whereby the maximum achievable layer thickness is specified at 30  $\mu\text{m}$ .

It is the object of the invention to create a further method of the type initially mentioned. In particular, the goal is to make it possible to produce without problems thicker layers with higher variability with regard to the coating structure, which in addition to the required hardness, corrosion resistance and adhesiveness in particular also possess a higher resistance to wear and tear and/or dielectric properties.

The invention solves this task by continuously increasing the amplitude values of the pulsed electrode voltage during the layer buildup supported by the electrical discharge at least in essence until reaching the desired layer thickness, in particular in the range of 30 to 300  $\mu\text{m}$  and preferably in the range of 50 to 250  $\mu\text{m}$ .

On the basis of this design, multifunctional layers of the most variable type can be manufactured in an especially sensitive manner, which not only adhere firmly to the substrate, but also which, in particular with regard to corrosion resistance and resistance to wear and tear, heat resistance as well as decorative surface refinement also have improved properties, and if necessary also possess dielectric properties, whereby at the same time even larger layer thicknesses can be achieved. The method can for example be used in the engineering and aircraft industry, in petrochemistry, radioelectric and medical industry as well as in the manufacture and surface refinement of merchandise.

The electrode voltage is preferably increased in such a way that in particular at least in essence a logarithmic time variation of the voltage amplitude takes place. For example, if barrier forming metals are being coated, an optimum adaptation to the increase of the thickness of the barrier layer is possible with such a voltage time curve

One particularly advantageous design variant of the method of the invention is characterized by the fact that the substrate forming the first electrode is alternately pulsed with an anodic and cathodic potential towards the second electrode. As a result, for example in the coating of barrier forming metals a continuous recharging of the electrical double layer is achieved, thus causing a depolarization.

Advantageously the anode voltage anodically pulsing the substrate is increased to a greater voltage value than the cathode voltage cathodically pulsing the substrate. As a result, particularly in the case of the application of oxidized layers to barrier forming metals and their alloys the unipolar conductivity of the oxidized layer is taken into account. Preferred voltage end values for the anode and cathode voltage are specified in Claims 8 and 9.

Preferred ranges for the current densities to select as well the temperature of the electrical bath and further advantageous design variants of the invention are specified in the dependent claims.

In the following the invention is described in greater detail using embodiments with reference to the drawing; the figures show the following:

Fig. 1 shows a purely diagrammatic view of a device for performing the method and

Fig. 2 shows a graphic representation of the measured microhardness and porosity of a multilayer in dependence on the layer depth

In Figure 1 a device for electrolytic coating of substrates or any other objects is shown in purely diagrammatic view.

In this case a container 14 filled with an electrolyte 12 is arranged in a water-cooled bath 10, with a mixer 16 extending into the container, by means of which the electrolyte 12 can be stirred.

The water-cooled bath 10 can be connected to a cooling-water circuit by means of valves 18.

The container 14 holding the electrolyte 12 has an electric supply facility 20 allocated to it, whose output terminals are connected on the one hand with the substrate 22 dipped in the electrolyte 12 and on the other hand with the container 14. Accordingly during the electrolytic coating the substrate 22 is used as the first electrode and the container 14 is used as the second electrode, between which a corresponding current flows on the basis of the applied electrode voltage.

The electric supply facility 20 comprises a voltage source 26 that can be connected to an AC voltage network by means of a switch 24 as well as a unit 28, by means of which the anode and cathode currents of the circuit containing the substrate 22 alternately pulsed with anodic and cathodic potential can be variably adjusted.

The electric supply facility 20 has a measuring unit 30 allocated to it, to which a recording unit 32 is separately connected, in order to be able to record the electrode voltages and currents occurring during the electrolytic coating.

A connection of the voltage source 26 to the AC voltage network is only possible when both the mixer 16 is switched on and the cooling-water circuit is switched on by means of the valves 18.

In the following the electrolytic coating method that can be performed for example by means of the described device is described in greater detail.

This method can, for example, be used for coating of electrical conducting metals, barrier forming metals as well as their alloys, whereby preferably an electrolytic bath having mainly a weak caustic reaction is used, which advantageously contains hydroxides and/or dissolving salts of weak acids, in particular such as silicates, aluminates, molybdates, phosphates and/or the like.

The object to be coated, for example a substrate, is dipped into the electrolytic bath. Then a voltage is generated between the substrate forming a first electrode and a second electrode also exposed to the first electrolyte. This voltage is then increased until a uniform spark and microarc discharge ensues on the surface of the substrate.

In addition, the voltage is also continuously increased during the layer buildup until the desired layer thickness is achieved. This voltage is generated alternately by means of anode and cathode pulses, which preferably have mildly rising and mildly falling edges and in particular at least in essence have an approximate sinusoidal wave shape. During the layer buildup the amplitude values increase corresponding to an at least in essence logarithmic regularity until an anode voltage of about 300 V to 800 V, preferably 300 V to 750 V and a cathode voltage of about 15 V to 400 V, preferably 15 V to 350 V have been achieved respectively.

The current densities for the alternating occurring anode and cathode currents lie in a range of about 1 A/dm<sup>2</sup> to 50 A/dm<sup>2</sup>, whereby lower values of the current density in particular in connection with the achievement of greater layer thicknesses are of significance. The temperature of the electrolytic bath is preferably selected in such a way that the liquid state of the bath is guaranteed, whereby the temperatures are advantageously kept in the range between 12° C and about 50° C. The container holding the electrolyte is advantageously made of stainless steel and can serve as the second electrode.

The object to be coated, for example a substrate, can be surrounded by an insulated electrical wire, which is to be connected with the corresponding connection of the electrical supply facility.

By using an electrolyte having mainly a caustic reaction for manufacturing of oxide layers supported by a surface discharge of the invention, it is possible to achieve particularly thick layers as well as further increase the quality of the layer.

By using a container made of stainless steel to hold the electrolyte the danger of an electrochemical decomposition of this second electrode as well as the danger of a contamination of the electrolyte is reduced to a minimum. The current density at the second electrode is significantly lower than at the first electrode. The electrolyte containing for example hydroxides and/or dissolving salts of weak acids, such as

silicates, aluminates, molybdates, phosphates and/or the like is for example mixed thoroughly by the mixer or stirrer.

As a result of the electrolysis of oxygen formed by water and hydrogen, it is siphoned advantageously. On the basis of the at least in essence logarithmic time voltage increase a relatively sensitive layer buildup results. The voltage time curve can be adapted to the increase in the barrier layer thickness as well as its breakdown voltage. Further, the alternating anode and cathode pulses cause a continuous recharging of the electrical double layer, which is accompanied by a depolarization.

The result is a high-quality coating, which has a special quality in particular with regard to density, hardness, resistance to wear and tear, breakdown voltage, heat resistance, adhesiveness etc.

The limits of the ranges specified for the amplitude values of the anode and cathode voltages can in particular be predetermined by the following parameters:

The lower limit can be determined by the minimum strength of the coating, as is predetermined by the user. The upper limit is predetermined by such spark and microarc ignitions or discharges, which would lead to a melting through or another type of non-treatable damage of the layer.

The big difference between the voltage values of the cathode voltage and those of the anode voltage can be explained by the unipolar conductivity of the oxidized layers for example applied to barrier layer forming metals and their alloys.

The method can for example be used for electrolytic formation of glass-like layers on barrier layer forming metals of the following group as well as their alloys: Mg, Ta, Ti, Nb, Ca, Zr, Hf, La, Mn, Al, Ru, V, Fe, Ni, Cr, and Co.

Figure 2 shows the changes resulting from the layer depth in the microhardness as well as the porosity of a multilayer coating of an Al object. On the abscissa the layer thickness is specified, whereby the analyzed coating comprises an intermediate layer with a thickness of 3-5  $\mu\text{m}$ , a main and function layer with a thickness of 150-250  $\mu\text{m}$  and a technological layer with a thickness of 30-100  $\mu\text{m}$ . The microhardness is laid off on the left ordinate, while the porosity is laid off on the right ordinate as a percentage.

Furthermore, in Figure 2 the composition of each of the relevant layers is specified. For analysis, the multilayer was taken down by means of grinding, whereby the hardness was measured by means of a microhardness meter. The composition of the different layers of the coating was determined by means of an x-ray phase analyzer. The porosity was recorded by means of stereometric metallography.

The technological layer of the coating, which was of poorer mechanical property as well as having a high porosity, contributes to the formation of the high-grade main and function layer. During the final treatment this technological layer can be ground off if such a layer is for example not required for achieving a particularly heat-resistant coating.

As a result, multifunctional layers of significantly higher quality than previously can be manufactured with the method of the invention.

#### Patent Claims

1. Method for electrolytic coating of substrates or the like, in which the substrate is dipped into an electrolytic bath and a current is generated between the substrate forming a first electrode and a second electrode, whereby the pulsed electrode voltage is boosted to a value in which an electric spark discharge and microarc discharge ensue on the substrate surface, characterized by the fact that the amplitude values of the pulsed electrode voltage are continuously increased during the layer buildup supported by the electrical discharge at least in essence until reaching the desired layer thickness, in particular in the range of 30 to 300  $\mu\text{m}$  and preferably in the range of 50 to 250  $\mu\text{m}$ .
2. Method according to Claim 1, characterized by the fact that the electrode voltage is increased in such a way that in particular at least in essence a logarithmic time variation of the voltage amplitude takes place.
3. Method according to Claim 1 or 2, characterized by the fact that the substrate forming the first electrode is alternately pulsed with an anodic and cathodic potential towards the second electrode.

4. Method according to one of the preceding claims, characterized by the fact that the electrode voltage is generated alternately by means of anode and cathode pulses, which preferably have mildly rising and mildly falling edges and in particular have an approximate sinusoidal wave shape.
5. Method according to one of the preceding claims, characterized by the fact that the pulse frequencies are selected in a range of 10 to 500 Hz and preferably in the range of 40 to 60 Hz.
6. Method according to one of the preceding claims, characterized by the fact that the setting of the current density takes place by means of a capacitive and/or inductive and/or ohmic variation of the impedance of the electrical supply source.
7. Method according to one of the preceding claims, characterized by the fact that the anode voltage anodically pulsing the substrate is increased to a greater voltage final value than the cathode voltage cathodically pulsing the substrate.
8. Method according to Claim 7, characterized by the fact that the anode voltage is increased to a voltage value of about 300 V to 800 V, preferably to about 300 V to 750 V.
9. Method according to Claim 7 or 8, characterized by the fact that the cathode voltage is increased to a voltage value of about 15 V to 400 V, preferably to about 15 V to 350 V.
10. Method according to one of the preceding claims, characterized by the fact that the current density of the anode and cathode currents is kept in a range of 1 A/dm<sup>2</sup> to 50 A/dm<sup>2</sup>, preferably 2 A/dm<sup>2</sup> to 20 A/dm<sup>2</sup>,
11. Method according to one of the preceding claims, characterized by the fact that the temperature of the electrolytic bath is kept in a range guaranteeing the liquid state of the bath and preferably in the range between 12° C and 50° C.
12. Method according to one of the preceding claims, characterized by the fact that an electrolytic bath having mainly a weak caustic reaction is used, which preferably contains hydroxides of the caustic metals and/or dissolving salts of weak acids, in particular such as silicates, aluminates, molybdates, phosphates and/or the like.
13. Method according to one of the preceding claims, characterized by the fact that the second electrode for the electrolytic bath is formed by a container preferably made of stainless steel.
14. Method according to one of the preceding claims, characterized by the fact that it is used for the coating of substrates or the like which consist of electric conducting metals, barrier forming metals and/or alloys and/or on which layers of these materials are provided.
15. Method according to one of the preceding claims, characterized by the fact that the duration of the preferably at least approximate sinusoidal wave shape pulses is selected in the range of about 1 ms to 20 ms.
16. Method according to Claim 15, characterized by the fact that the duration of the anodic pulses is selected in the range of about 10 ms to 15 ms and the duration of the cathodic pulses is selected in the range of about 5 ms to 10 ms.

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Fig. 1

Fig. 2

MICROHÄRTE = MICROHARDNESS

PORÖSITÄT = POROSITY

ZWISCHENSCHICHT – INTERMEDIATE LAYER

HAUPT UND FUNKTIONSSCHICHT = MAIN AND FUNCTION LAYER

TECHNOLOGISCHE SCHICHT = TECHNOLOGICAL LAYER



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(71) Anmelder: Hauzer, Franciscus Johannes  
Matheus  
Koelderstraat 21  
NL-5916 NH Venlo(NL)

(72) Erfinder: Mitin, Boris Sergejevitsj  
ul. Mikloecho-Maklaja, d.41, kv.113  
Moskau(RU)

Erfinder: Suminov, Igor Vjatsjeslavovits  
ul. Sjtsjebakovskaja, d.8-12, kv.55  
Moskau(RU)

Erfinder: Epelfeld, Andre Valerjevitsj  
Leningradskoje sjoss d.9 k.2, kv.326  
Moskau(RU)

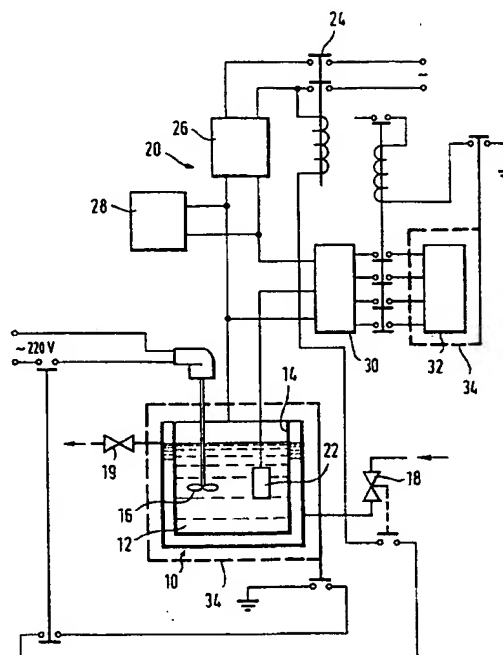
Erfinder: Fjodorov, Jevgenij Aleksandrovitsj  
ul. Verchojanskaja, d.6, k.1, kv.63  
Moskau(RU)

(74) Vertreter: Morgan, James Garnet et al  
Manitz, Finsterwald & Rotermund  
Patentanwälte  
Postfach 22 16 11  
D-80506 München (DE)

(54) Verfahren zur elektrolytischen Beschichtung von Substraten und dergleichen.

(57) Es wird ein Verfahren zur elektrolytischen Beschichtung von Substraten oder dergleichen beschrieben, bei dem das jeweilige Substrat in ein elektrolytisches Bad getaucht und zwischen dem eine erste Elektrode bildenden Substrat und einer zweiten Elektrode ein Strom erzeugt wird. Die Elektrodenspannung wird zunächst auf einen Spannungswert angehoben, bei dem sich an der Substratoberfläche eine elektrische Funken- und Mikrobogenentladung einstellt. Die Elektrodenspannung wird auch während des durch die elektrische Entladung unterstützten Schichtaufbaus kontinuierlich erhöht, bis die gewünschte Schichtdicke erreicht ist.

Fig.1



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